1	Performance modulation and optimization of PE						
2	fiber reinforced 3D-printed geopolymer						
3 4	Xingyi Zhu ^a , Jiakang Wang ^a , Ming Yang ^a , Jianzhuang Xiao ^b , Yating Zhang ^{c*} , Francisco A. Gilabert ^d						
5	^a Key Laboratory of Road and Traffic Engineering of the Ministry of Education, Tongji University, Shanahai 200092 P.R.China						
7 8	^b Department of Structural Engineering, College of Civil Engineering, Tongji University, Shanghai, 200092. P R China						
9 10 11	^c Jiangsu Key Laboratory of Advanced Food Manufacturing Equipment and Technology, School of Mechanical Engineering, School of Environmental and Civil Engineering, Jiangnan University, Wuxi, 214122, P R China						
12 13	^d Department of Materials, Textiles and Chemical Engineering, Ghent University, Tech Lane Ghent Science Park - Campus A, Technologiepark-Zwijnaarde 46, 9052 Zwijnaarde, Belgium						
14	Abstract: This paper aims to develop an environmentally friendly and low-carbon geopolymer for						
15	3D printing, which has excellent mechanical and rheological performance. The effect of ground						
16	granulated blast furnace slag (GGBS), NaOH and sand on mechanical strengths, 3D printing						
17	performance and rheological behavior was investigated to determine the optimum mix proportion						
18	for 3D-printed geopolymer. Moreover, polyethylene (PE) fibers were introduced to reinforce the						
19	performance of 3D-printed geopolymer. Results show that when the ratio of GGBS, NaOH and						
20	sand is 1:0.13:2.67, geopolymer exhibits superior mechanical, 3D printing and rheological						
21	properties. Increasing the dosage of GGBS and sand leads to an overall increase in the yield stress						
22	but a decrease in the consistency coefficient, indicating that it benefits the stacking and fluidity						
23	performance of 3D-printed geopolymer. However, with an increase of NaOH content, the stacking						
24 95	performance increases while the fluidity decreases. Although increasing NaOH and sand content						
20 26	benefits the viscosity recovery performance, an increase in GGBS content has an opposite effect.						
20 97	and 21.3% in 7 d and 28 d flexural strength respectively given a PE fiber volves of 0.6%						
21 28	Increasing the volume of PE fibers leads to a significant rise in the stacking performance but a						
20 29	reduction in the fluidity Furthermore adding PF fibers negatively affects the geopolymerization						
30	but benefits the hydration process given an increase of Si/Al and Si/Ca ratio identified in PF fiber						
31	reinforced 3D-printed geopolymer.						
32	Keywords: Geopolymer, 3D printing, PE fiber, Mechanical property, Rheological property						

^{*} Corresponding author: ytzhang@jiangnan.edu.cn

1. Introduction

3D printing, also known as additive manufacturing, provides a sustainable way to produce three-dimensional building components in a precise shape even with complex geometries, which significantly reduces material waste and thus, contributes to cost savings and lower energy consumption [1-3]. Considering the significant amount of carbon emission and energy consumption from the production of traditional cement-based materials [4], which are main construction materials for 3D printing, low-carbon cementitious materials such as alkali-activated geopolymers have gained extensive attention. McLellan et al. [5] found that geopolymers were more environmentally friendly than cement-based materials as their global warming potential (GWP) was 62% lower than that of cement-based materials. Similarly, Turner and Collins [6] reported that producing geopolymers reduced the acidification potential (AP) and eutrophication potential (EP) by over 20%.

As a primary coal-based waste, fly ash is rich in silicoaluminates, which makes it an effective raw material for alkali-activated geopolymers [7-11], and it can be expected that the performance of geopolymer is significantly correlated with the decomposition of Si and Al elements from fly ash [12,13]. Ge et al. [14] pointed out that only 10% of fly ash was possibly involved in geopolymerization, providing an opportunity for other additives such as ground granulated blast furnace slag (GGBS) to improve geopolymer performance [15]. Although adding GGBS has a limited impact on Si/Al and Na/Al molar ratios, it significantly increases the Ca/Si molar ratio in geopolymer, leading to improved mechanical properties [16]. Unfortunately, Singh et al. [17] found that incorporating GGBS negatively affected the workability of fresh geopolymer. Therefore, the determination of GGBS dosage needs to balance its opposing effects on mechanical properties and workability. Similarly, alkaline-activator and sand are also important indicators affecting the performance of geopolymers [18,19]. Chindaprasirt et al. [20] demonstrated that increasing the concentration of sodium silicate and NaOH resulted in a decline in the flowability of geopolymer mortar. They suggested a sodium silicate to NaOH ratio between 0.67 and 1.0 to produce high-strength geopolymer. Adding sand contributes to a reduction in porosity and benefits the viscosity of geopolymer, thus resulting in a robust skeleton structure and enhanced mechanical strengths [21]. As expected, the mix proportion of different materials can have a profound effect on geopolymer performance. Abdulrahman et al. [22] identified that increasing the alkaline-activator to binder ratio led to a reduction in mechanical strengths. Panda and Tan [23] investigated the influence of different mix proportions of fly ash, GGBS, sand and alkaline reagent on the extrudability, shape retention, buildability and open time of geopolymers for 3D printing. However, mechanical properties were not considered when determining the mix proportion of 3D-printed geopolymer in their study. In fact, it is widely accepted that fly ash-based geopolymers have poor toughness and lower flexural strength, thereby extensive studies have adopted fibers to enhance the flexural performance of geopolymers [24-26]. Among different fibers, polyethylene (PE) fiber is recognized as a cost-effective and corrosion-resistant fiber, which can positively affect strengths, toughness and crack resistance of geopolymer. Ren and Li [27] demonstrated that the correlation between flexural toughness, equivalent flexural strength and PE fiber reinforcement index was quadratic. Hu et al. [28] identified that PE fiber factor had a significant impact on the compressive and flexural strength of geopolymer and suggested that a fiber factor of less than 150 benefited the mechanical performance of geopolymer. Unfortunately, PE fiber

reinforced geopolymer for 3D printing has gained little attention.

Furthermore, owing to the absence of vibration and compaction of 3D-printed components, the geopolymer for 3D printing has a higher requirement on rheological properties [29,30]. Li et al. [31] indicated that the static rheological behavior of geopolymers conformed to a Bingham model. With the incorporation of GGBS, the shear stress significantly enhanced. Alanazi et al. [32] found that the flowability of geopolymer decreased as additive (i.e., GGBS and silica fume) replacement ratio and sodium silicate to NaOH ratio increased. Similarly, Nath and Sarker [33] identified that incorporating GGBS into fly ash-based geopolymers resulted in a decline in the workability and setting time and the more the GGBS, the lower the slump. However, increasing alkaline liquid content caused an increase in workability and setting time and a reduction in compressive strength, with the optimum sodium silicate to NaOH ratio being 2.5. Jaji et al. [30] summarized the workability and rheological performance of 3D-printed geopolymer and fit the rheological curves using the Bingham model. Although above studies provide evidence for the feasibility of using fly ash-based geopolymer for 3D printing, there is still a lack of multi-parameter research on the rheological properties of 3D-printed geopolymer considering the effects of GGBS replacement ratio, NaOH and sand content and PE fiber volume.

This study aims to develop a 3D-printed geopolymer with superior rheological and mechanical properties. An orthogonal experiment was conducted to determine the optimum GGBS, NaOH and sand content for 3D-printed geopolymer considering both mechanical and 3D printing performance. The influence of GGBS, NaOH and sand on the rheological behavior of 3D-printed geopolymer was further explored. In addition, PE fibers were introduced to enhance the mechanical performance of 3D-printed geopolymer. The influence of PE fiber on mechanical strengths, rheological performance, structure morphology and chemical composition of gel products of 3D-printed geopolymer was investigated considering various fiber volumes.

2. Materials and methods

2.1 Raw materials

In this study, fly ash (from Hebei Yiran Product Processing Plant), GGBS (from Hebei Yiran Product Processing Plant), manufactured sand (from Hebei Shengxiang Sand Product Processing Plant) and PE fiber (from Hangzhou Quanli Science and Technology Co., Ltd), as shown in Fig. 1, were used as raw materials to prepare 3D-printed geopolymer. The compositions of fly ash and GGBS and the physical properties of PE fiber are summarized in Table 1 and Table 2, respectively. The particle size distribution of fly ash and GGBS is shown in Fig. 2. In addition, the alkaliactivator adopted herein was made of sodium silicate solution (from Tianjin Zhonghe Shengtai Chemical Co., Ltd.), NaOH (from Aladdin Reagent Co., Ltd.) and water. The original modulus of sodium silicate solution is 3.1 and the purity of NaOH is higher than 98%. The proportion of the compositions of sodium silicate solution is demonstrated in Table 3.

114	Tabl	e 1 Chen	nical cor	npositio	ns of fly	ash an	d GGBS	•		
	Chemical composition	SiO_2	Al_2O_3	CaO	MgO	K ₂ O	Fe ₂ O ₃	TiO ₂	Na ₂ O	SO_3
	Fly ash (%)	52.74	33.02	4.12	0.52	1.53	5.02	2.16	0.33	0.22
	GGBS (%)	30.74	17.48	41.02	4.32	0.35	1.21	2.04	0.12	2.53



The experiment in this study consists of three parts. First, the optimum mix proportion of 3Dprinted geopolymer was determined through an orthogonal test, considering the effects of GGBS dosage, modulus of alkaline solution and sand content on compressive strength, flexural strength and 3D printing performance. The dosage range for different raw materials was determined based on the results of preliminary experiments and previous findings in the literature [34-37]. Specifically, three GGBS dosages, i.e., 100, 200 and 300 g (named A1, A2 and A3 level, respectively), were designed as a substitute for fly ash, and three modulus of alkaline solution, i.e.,

0.75, 1.00 and 1.25, were selected, which were achieved by changing the NaOH content to 27, 39
and 58 g, respectively (named B1, B2 and B3 level, respectively). In addition, three sand contents,
i.e., 400, 600 and 800 g (named C1, C2 and C3 level, respectively), were selected. The designed
L9 orthogonal test is shown in Table 4.

Table 4 The scheme of the orthogonal test.							
Test group	Fly ash (g)	GGBS (g)	NaOH (g)	Sand (g)	Sodium silicate solution (g)	Water (g)	
1	900	100 (A1)	27 (B1)	400 (C1)	176.9	190.9	
2	800	200 (A2)	27 (B1)	600 (C2)	176.9	190.9	
3	700	300 (A3)	27 (B1)	800 (C3)	176.9	190.9	
4	800	200 (A2)	39 (B2)	400 (C1)	176.9	190.9	
5	700	300 (A3)	39 (B2)	600 (C2)	176.9	190.9	
6	900	100 (A1)	39 (B2)	800 (C3)	176.9	190.9	
7	700	300 (A3)	58 (B3)	400 (C1)	176.9	190.9	
8	900	100 (A1)	58 (B3)	600 (C2)	176.9	190.9	
9	800	200 (A2)	58 (B3)	800 (C3)	176.9	190.9	

Secondly, the effect of key factors, i.e., GGBS dosage, modulus of alkaline solution and sand content, on the rheological behavior of 3D-printed geopolymer was investigated. The impact of a single factor (i.e., GGBS, NaOH and sand content) on rheological properties can be evaluated by fixing the content of the other two factors to the optimal content obtained through the orthogonal test. Thirdly, PE fibers were introduced to improve the mechanical and rheological performance of 3D-printed geopolymer. A total of four volumes of PE fibers, i.e., 0%, 0.2%, 0.4%, and 0.6%, were selected to assess the reinforcing effect of PE fibers on 3D-printed geopolymer.

2.3 Experimental methods

2.3.1 Preparation of 3D-printed geopolymer

The preparation process of 3D-printed geopolymer is demonstrated in Fig. 3. Before mixing, the alkali solution was pre-formulated. The NaOH pellet was first dissolved in water with a stirring time of 2 min before mixing with sodium silicate solution for another 5-min stirring. Then the alkaline solution was poured into a plastic container for 6 h until it cooled for later use. Afterward, raw materials, i.e., fly ash, GGBS and sand, were added to the mixer following the designed mix proportion listed in Table 4 and experienced a 1-min dry mixing. The alkali solution was then added to the mixer with a 3-min fast mixing. After the geopolymer slurry was fully mixed, the fresh geopolymer was then poured into the silo of the 3D printer for multi-layer printing. The nozzle of the 3D printer had a diameter of 30 mm. The printing and extrusion speed was set to 0.012 and 0.036 m/s, respectively. After printing, 3D-printed geopolymer specimens were placed in the laboratory environment at a room temperature of $20 \sim 25$ °C and a relative humidity of 55 ± 5 % for 48 h before cutting to the size of $40 \times 40 \times 40$ mm and $40 \times 40 \times 160$ mm. To simulate a real 3D printing environment, the printed specimens were continually cured in the laboratory environment for further tests.



Fig. 3 Preparation of 3D-printed geopolymer specimen.

159 2.3.2 Mechanical tests

160 The influence of GGBS dosage, modulus of alkaline solution, sand content and PE fiber 161 volume on the compressive and flexural strength of 3D-printed geopolymer after 7 and 28 days of 162 curing was investigated. The size of the specimen for compressive and flexural tests was $40 \times 40 \times$ 163 40 mm and $40 \times 40 \times 160$ mm, respectively. Following GB/T 17671-2021 [38], the loading rate 164 for compressive and flexural tests was set to 2400 and 50 N/s, respectively. The test scheme for 165 mechanical tests is shown in Fig. 4.



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Fig. 4 Scheme for mechanical tests: (a) testing machine, (b) compressive and (c) flexural fixture.

2.3.3 3D printing performance

To evaluate the effects of GGBS, NaOH and sand on the 3D printing performance of the designed geopolymer, the variations in the stacking performance of different geopolymers were investigated. The shape retention coefficient, defined in Eq. 1, was used herein to characterize the stacking performance of 3D-printed geopolymer.

$$\alpha = \frac{H_f}{H_i} \tag{1}$$

174 where α is the shape retention coefficient of the 3D-printed specimen, H_i is the height of the 175 specimen at the initial printing (i.e., just after 3D printing) and H_f is the height of the specimen 176 after final solidification (i.e., 1 h after 3D printing), as shown in Fig. 5. It is worth mentioning that 177 both H_i and H_f were measured three times at different locations and the average value was adopted 178 to calculate the shape retention coefficient.





181 2.3.4 Rheology tests

Shear rate scanning test and three-phase test (3ITT) were conducted, using Anton Paar MCR302 dynamic shear rheometer and CC17 cylindrical spindle with a diameter of 17 mm, on 3D-printed geopolymer to assess the sensitivity of rheological properties upon the variation in the contents of GGBS, NaOH, sand and PE fiber. Representative curves of rheology tests are presented in Fig. 6. For shear rate scanning test, the shear rate varied linearly from 0 to 100 s⁻¹ over time (i.e., 0 to 200 s) to obtain the curve of shear stress versus shear rate [39,40]. The reason for selecting this range for the shear rate is that it covers the typical shear rates that materials may experience during mixing and printing processes, providing a comprehensive information on rheological properties of geopolymer paste. The Herschel-Bulkley (H-B) model, which is applicable to fit non-Newtonian fluids given a certain yield stress [41,42], was adopted herein to fit the curve. Then the rheological properties can be obtained, i.e., yield stress, consistency coefficient and flow index, as defined in Eq. 2.

$$\tau = \tau_0 + b\gamma^k \tag{2}$$

where τ and γ are shear stress and shear rate, respectively, and τ_0 , *b* and *k* are yield stress, consistency coefficient and flow index of fresh geopolymer, respectively. A higher τ_0 suggests enhanced stackability of the geopolymer and a larger *b* indicates poor flow characteristics. While *k* describes the degree of shear-thinning or shear-thickening behavior. If k < 1, the fluid can be characterized as shear-thinning, and if k > 1, the fluid becomes shear-thickening, exhibiting increased viscosity under shear stress.

For three-phase test, the shear rate of $0.01 - 100 - 0.01 \text{ s}^{-1}$ was selected [43,44]. In the first stage, the shear rate was set to 0.01 s^{-1} with a duration of 60 s, which was used to simulate the static state of geopolymer slurry after placing it in the storage bin of the 3D printer after mixing. In the second stage, a shear rate of 100 s^{-1} and a duration of 10 s were set to simulate the extrusion of geopolymer from the nozzle of the 3D printer. In the third stage, the shear rate was set back to 0.01 s^{-1} with a duration of 60 s. This was to simulate the stacking and molding process of geopolymer after being extruded from the nozzle. The viscosity recovery ratio, which is the ratio

208 of the viscosity during the third stage of shearing to the initial viscosity, as defined in Eq. 3, was 209 used to characterize the viscosity recovery performance after 3D printing.

 $\varepsilon = \frac{\eta_{III}}{\eta_I} \tag{3}$

where ε is the viscosity recovery rate of geopolymer paste, η_I is the viscosity of geopolymer at the end of the first stage (i.e., the mean value of 50 ~ 60 s) and $\eta_{\mathbb{Z}}$ is the viscosity of geopolymer during the third stage (i.e., the mean value of 95 ~ 105 s).



Fig. 6 Representative curves of (a) shear rate scanning test and (b) three-phase test.

2.3.5 SEM-EDS analysis

In this study, scanning electron microscopy (SEM) analysis was employed to assess the morphology of geopolymerization products and PE fibers in 3D-printed geopolymer. The adopted SEM equipment was ZEISS Gemini 300 field emission microscope with Inlens and ET secondary electron detectors. In addition, the variation in the elemental composition of the gel products in 3D-printed geopolymer with and without PE fibers was characterized through energy dispersive spectroscopy (EDS) equipped with OXFORD Xplore.

3. Results and discussions

3.1 Optimization design of 3D-printed geopolymer

3.1.1 Compressive strength

The compressive strength of designed 3D-printed geopolymers is presented in Fig. 7 (a). As expected, the mix proportion of GGBS, NaOH and sand has a profound impact on the compressive strength of 3D-printed geopolymer. The maximum 7-d and 28-d compressive strength (i.e., 41.9 and 44.5 MPa, respectively) is identified in Group 7 and Group 5, respectively. While the lowest 7-d and 28-d compressive strength is 11.6 and 12.4 MPa, respectively, which is identified in Group 8 and Group 2, respectively. Fig. 7 (b) presents the compressive strength effect curve of 3D-printed geopolymer. Both GGBS and NaOH content have a positive correlation with compressive strength given that the more the GGBS and NaOH content, the higher the mean compressive strength. However, with the increase of sand, the compressive strength experiences a decrease before increasing. In addition, it can be noted that the increase in GGBS content from A2 (i.e., 200 g) to A3 (i.e., 300 g) level has a more significant influence on compressive strength than the increase from A1 (i.e., 100 g) to A2 (i.e., 200 g) level. Considering that GGBS has a higher

CaO content than fly ash (see Table 1), the content of Ca²⁺ increases with more GGBS substituting fly ash, which indicates a higher Ca/Si ratio. According to previous studies, a higher Ca/Si ratio is conducive to the formation of C-(A)-S-H gel, making C-(A)-S-H and N-A-S-H gel coexist in the system [45,46]. These gel products are effectively bonded with unreacted particles, dehydrated and hardened to form a dense structure, thereby positively affecting the compressive performance of 3D-printed geopolymer [47]. Based on the compressive strength effect curve, it can be indicated that the optimum mix ratio for 7-d and 28-d compressive strength is A3B3C3 and A3B2C3, respectively.



Fig. 7 (a) Compressive strength and (b) compressive strength effect curve of 3D-printed geopolymer.

The result of the range and variance analysis of compressive strength is shown in Table 5. Apparently, GGBS content has the most significant influence on compressive strength, because it has the highest range, i.e., 20.35 and 15.84, for 7-d and 28-d strength, respectively. The least influential factor is sand content, with a range of 7.22 and 1.33 for 7-d and 28-d compressive strength, respectively. Similar findings can be obtained from variance results. A higher F-ratio of GGBS content indicates a higher contribution of GGBS to compressive strength. Although NaOH content has a limited impact on 7-d compressive strength, it has a greater impact on 28-d

compressive strength. Given that the F-ratio of sand content is small for both 7-d and 28-d compressive strength, the optimum mix proportion considering the compressive performance of 3D-printed geopolymer can be obtained based on the effect of GGBS and NaOH content. Therefore, the mix proportion of A3B2Ci (i=1, 2, 3) with a GGBS content of 300 g and a NaOH content of 39 g is suggested herein.

		8	····· ·	I	9	
Factor	7-d c	ompressive stre	ength	28-d o	compressive str	rength
Factor	GGBS	NaOH	Sand	GGBS	NaOH	Sand
Range	20.35	7.89	7.22	15.84	13.50	1.33
F-ratio	7.93	1.11	0.84	3.84	2.84	0.02

Table 5 Range and variance analysis of compressive strength.

3.1.2 Flexural strength

Fig. 8 (a) presents the flexural strength of designed 3D-printed geopolymers. Expectedly, the sensitivity of flexural strength from the variation of GGBS, NaOH and sand contents is significant given that the maximum 7-d and 28-d flexural strength is found to be 8.16 and 9.55 MPa, respectively, while the minimum 7-d and 28-d strength is 2.41 and 2.16 MPa, respectively. Similarly, the difference between 7-d and 28-d flexural strength given the same mix proportion is also limited. The effect curve of flexural strength is exhibited in Fig. 8 (b). When GGBS content increases from A1 to A3, the 7-d flexural strength shows a continuous increase, but the 28-d strength increases first and then decreases. On the contrary, given an increase in the NaOH content, the 7-d and 28-d flexural strength exhibits opposite patterns. It suggests that excessive or insufficient alkaline content can result in a reduction in early-age flexural strength. Increasing NaOH content benefits the dissolution of silicon and aluminum in fly ash and GGBS, which is conducive to the geopolymerization to promote the production of amorphous gel to fill the pores and to make geopolymer dense [48,49], responsible for an increase in flexural strength. However, adding massive NaOH indicates excessive OH⁻ in the system, which results in more gel products in the initial stage of geopolymerization [50]. These gels precipitate and harden rapidly, which hinders further dissolution of aluminosilicates, thus having a negative impact on flexural strength. Furthermore, as the sand content increases, the 7-d flexural strength increases persistently but the 28-d flexural strength experiences a sharp decrease before a rebound. Based on the effect curve, the mix proportion of A3B2C3 and A2B3C3 can be recommended considering 7-d and 28-d flexural strength, respectively.



Fig. 8 (a) Flexural strength and (b) flexural strength effect curve of 3D-printed geopolymer.

Table 6 lists the range and variance results of flexural strength. For 7-d flexural strength, sand content exhibits the most prominent influence given a range of 2.46, followed by NaOH content given a range of 2.23. Unlike compressive strength, the effect of GGBS content on the 7-d flexural strength of 3D-printed geopolymer is less significant. The results indicate that among these factors, sand content is the determinant factor for the 7-d flexural strength. Sand can effectively bear loads and suppress crack propagation and the dissolution of partial sand particles benefits the interface bond between sand and the geopolymer mortar [51], thereby enhancing the early-age flexural strength of 3D-printed geopolymer. When it comes to 28-d strength, NaOH content becomes the dominant factor given a range of 2.76, followed by sand content. Similar to 7-days results, GGBS content is the least impactful factor on 28-d flexural strength. As observed in Table 6, the variance of different factors is overall consistent with the range result. However, considering that the F-ratio of all three factors for 7-d flexural strength is relatively small, the impact of GGBS, NaOH and sand content on 7-d flexural strength can be neglected. Therefore, the priority of three factors for flexural strength can be determined based on their impact on 28-d strength, i.e., NaOH content > sand content > GGBS content, and the optimum mix proportion is suggested as AiB3Ci with a

		0	ť		0	
Factor	7-0	l flexural streng	gth	28-	d flexural stren	ngth
Factor	GGBS	NaOH	Sand	GGBS	NaOH	Sand
Range	1.55	2.23	2.46	1.12	2.76	2.21
F-ratio	0.36	0.88	1.20	0.57	4.59	2.61

Table 6 Range and variance analysis of flexural strength.

3.1.3 3D printing performance

The shape retention coefficient of designed 3D-printed geopolymers is presented in Fig. 9 (a). Group 3 and Group 5 with a mix ratio of A3B1C3 and A3B2C2, respectively, have better 3D printing performance given a shape retention coefficient of up to 0.925. The poorest 3D printing performance with a minimum shape retention coefficient of 0.833 is identified in Group 8 with a mix ratio of A1B3C2. The shape retention coefficient effect curve is shown in Fig. 9 (b). All three factors have a linear relationship with the shape retention coefficient. Specifically, the shape retention coefficient positively correlates to GGBS and sand content, but negatively correlates to NaOH content. It indicates that increasing GGBS and sand contents benefits the 3D printing performance of geopolymers. As mentioned earlier, adding GGBS benefits the compactness of geopolymer due to the increased C-(A)-S-H gel, thereby leading to improved stacking performance of 3D-printed geopolymer. Additionally, adding sand enhances the packing density and reduces porosity of 3D-printed geopolymer, and it increases the interparticle friction and stress distribution by strengthening the aggregate-mortar interface [51], which enhances the yield stress of 3D-printed geopolymer, thereby resulting in a higher shape retention coefficient. However, increasing NaOH content accelerates the dissolution of fly ash and GGBS particles, producing a large amount of amorphous gel which adheres to and precipitates on the surface of unreacted particles [52,53]. Therefore, the early-age geopolymerization and hydration reaction will be retarded, which can negatively affect the stackability and buildability of 3D-printed geopolymer, thus deteriorating the 3D printing performance. According to the effect curve of shape retention coefficient, it can be assumed that the optimum mix for 3D printing performance is A3B1C3.



Fig. 9 (a) Shape retention coefficient and (b) shape retention coefficient effect curve of 3Dprinted geopolymer.

The range and variance results are presented in Table 7. GGBS content has the highest range and F-ratio, indicating that 3D printing performance is most sensitive to GGBS content. The second and third sensitive factors are sand content and NaOH content. Smaller F-ratios indicate that the impact of all three factors (GGBS, NaOH, and sand content) on 3D printing performance is minimal. Nonetheless, trends can still be discerned, that is, the shape retention coefficient increases with the increase of GGBS and sand content as well as the decrease of NaOH content, which can be adopted to further finalize the optimum mix of geopolymer for 3D printing.

 Table 7 Range and variance analysis of shape retention coefficient.

Factor	GGBS	NaOH	Sand
Range	0.04	0.03	0.03
F-ratio	0.63	0.38	0.48

3.1.4 Optimum mix proportion

From the discussion in section 3.1, it can be concluded that the mix proportion of GGBS, NaOH and sand content has a remarkable influence on both the mechanical and 3D printing performance of 3D-printed geopolymer. For compressive and flexural strength, the dominant factor is GGBS content and NaOH content with the optimum dosage at the A3 level (i.e., 300 g) and B2/B3 level (i.e., 39 or 58 g), respectively. However, a NaOH content of 58 g leads to a sharp decrease in the shape retention coefficient, resulting in poor 3D performance. Therefore, the NaOH content at the B2 level (i.e., 39 g) is suggested herein for 3D-printed geopolymer. For sand content, the dosage at the C3 level (i.e., 800 g) is the optimum one for both mechanical properties and 3D printing performance. Hence, the sand content of 800 g is recommended herein for 3D-printed geopolymer. The compressive and flexural strength and shape retention coefficient of the optimum 3D-printed geopolymer are further tested, with the mean results and standard deviation (SD) shown in Table 8. Moreover, the suggested optimum content for GGBS, NaOH and sand (i.e., 300, 39 and 800 g, respectively) will be used for further investigation on the rheological behavior of 3D-printed geopolymer.

 Table 8 Mechanical and 3D printing performance given the optimum mix ratio.

Comp	Compressive strength (MPa) Flexural strength (MPa)				Shape re	etention			
7-	d	28-	d	7-	·d	28	-d	coeffic	ient α
Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
51.3	2.6	54.3	1.9	7.15	0.16	7.93	0.14	0.92	0.24

3.2 Rheological behavior of 3D-printed geopolymer

3.2.1 Mix proportion

With the suggested contents for GGBS, NaOH and sand (i.e., 300, 39 and 800 g, respectively) obtained in section 3.1, the influence of a single factor on the rheological behavior of 3D-printed geopolymer was investigated with the mix proportions and fitting results of H-B model listed in Table 9.

			Mix proportion	on			Fitting	results
Group	GGBS	Fly ash	Sodium silicate	Water	NaOH	Sand	ЪЭ	SD
	(g)	(g)	solution (g)	(g)	(g)	(g)	K2	3D
A1	100	900	176.9	190.9	39	800	0.9992	0.46633
A2	200	800	176.9	190.9	39	800	0.9999	0.23509
A3	300	700	176.9	190.9	39	800	0.99919	1.7118
B1	300	700	176.9	190.9	27	800	0.99908	1.4094
B2(A3)	300	700	176.9	190.9	39	800	0.99919	1.7118
B3	300	700	176.9	190.9	58	800	0.99986	0.80039
C1	300	700	176.9	190.9	39	400	1	0.14714
C2	300	700	176.9	190.9	39	600	0.9999	0.19596
C3(A3)	300	700	176.9	190.9	39	800	0 99919	1 7118

Table 9 Mix proportions and H-B model fitting results.

3.2.2 Yield stress

The effect of GGBS, NaOH and sand content upon the yield stress of 3D-printed geopolymer paste is significant, as shown in Fig. 10. Given an increase in GGBS content from 100 to 300 g, the yield stress initially increases and then decreases with the peak value being 57.86 MPa. Although increasing the GGBS content to 300 g leads to a slight decrease in the yield stress compared to the geopolymer with a GGBS content of 200 g, it is still higher than that of the

geopolymer with a GGBS content of 100 g. It indicates that adding GGBS benefits the stacking performance of geopolymer paste, consistent with previous studies [33]. As sand content rises, the yield stress of the fresh geopolymer undergoes a significant increase with the maximum value reaching 55.54 MPa at a sand dosage of 800 g. The reason for the positive impact of sand content on the stacking performance of 3D-printed geopolymer can be possibly related to the role of sands in geopolymer paste, that is, acting as aggregates to enhance the stability of geopolymer. Similarly, increasing NaOH content also contributes to a continuous increase in the yield stress. Adding alkali promotes geopolymerization, thus benefiting the stackability of geopolymer paste. However, it can be inferred that a sustained increase in NaOH content will have a limited effect on the stacking performance of geopolymer, considering that the increase in NaOH content from 39 to 58 g only causes a slight rise in the yield stress, i.e., from 55.54 to 57.78 MPa.





3.2.3 Consistency coefficient

Fig. 11 shows the impact of GGBS, NaOH and sand content on the consistency coefficient of 3D-printed geopolymer. As GGBS dosage increases, the consistency coefficient experiences a decrease before ascending. It indicates that the fluidity of geopolymer paste varies with GGBS content. When GGBS content increases to 200 g, the fluidity is significantly increased with the consistency coefficient being 3.65. However, when GGBS content further increases to 300 g, the fluidity of 3D printed geopolymer declines. With more GGBS substituting fly ash, the number of spherical particles (fly ash) in the paste decreases, which could cause a decrease in the fluidity. As sand content increases, the consistency coefficient of the paste consistently decreases, suggesting that increasing sand content benefits the fluidity of fresh geopolymer. This may be because sand particles can facilitate the movement between larger particles, acting as micro ball bearings that aiding in the fluidity of the mixture. The optimum geopolymer fluidity is achieved at a sand dosage of 800 g given that the lower the consistency coefficient, the better the fluidity. As expected, the fluidity of geopolymer paste decreases with an increase in NaOH content. When NaOH content increases from 27 to 58 g, the consistency coefficient of the fresh paste exhibits a progressive increase from 3.03 to 4.19.



Fig. 11 The consistency coefficient of 3D-printed geopolymer.

3.2.4 Flow index

The sensitivity of the flow index upon the variation of GGBS, NaOH and sand content is exhibited in Fig. 12. It can be noted that the flow index of all geopolymers is less than 1, indicating that the designed geopolymers are non-Newtonian fluids with shear-thinning properties, suitable for 3D printing. As presented in Fig. 12, the flow index of 3D-printed geopolymer paste increases with the rise of GGBS dosage. Given a GGBS content of 300 g, the thixotropic behavior of 3D-printed geopolymer comes closer to that of a Newtonian fluid. As sand content increases, the flow index decreases first and then increases but the variation is small (i.e., 2%). Therefore, it can be assumed that the impact of sand content on the thixotropic behavior of 3D-printed geopolymer paste is limited. In addition, the increase in NaOH content leads to a reduction in the flow index, which indicates that increasing NaOH content results in a more pronounced shear thinning behavior of 3D-printed geopolymer paste. The higher the NaOH content, the higher the intermolecular interactions, which causes accelerated geopolymerization and is responsible for the formation of numerous cross-linked cluster structures [54]. These molecular structures are prone to enhancing the shear-thinning behavior under shear stress, thus resulting in a lower flow index.







3.2.5 Viscosity recovery rate

Fig. 13 describes the correlation between the viscosity recovery rate and the content of GGBS, NaOH and sand. As shown in Fig. 13, the viscosity recovery rate of 3D-printed geopolymer undergoes a sharp increase and then decreases given an increase in GGBS content. When GGBS dosage is 200 g, the viscosity recovery rate peaks at 54.62% with an increase of 13.7%. It indicates that within a certain range, adding GGBS can effectively improve the viscosity recovery performance of geopolymer slurry after the shear damage during 3D printing. The ultra-fine GGBS particles can provide more Ca²⁺, which serves as nucleation sites to promote the rapid reconstruction of geopolymer gel network [55,56], thus increasing the rapid viscosity recovery after shear damage. In addition, a positive correlation between sand content and viscosity recovery performance can be identified given that the viscosity recovery rate increases as sand content rises. It indicates that increasing the amount of sand contributes to the restoration of the geopolymer's viscosity, thereby improving the stacking performance of fresh geopolymer after it is extruded from the nozzle during 3D printing. Similarly, it can be observed that the viscosity recovery rate also increases with the rise of NaOH content, implying that a higher NaOH dosage positively affects the stacking performance of 3D-printed geopolymer.



Fig. 13 The viscosity recovery rate of 3D-printed geopolymer.

Based on the above discussions of four rheological properties, i.e., yield stress, consistency coefficient, flow index and viscosity recovery rate, it can be concluded that the GGBS, NaOH and sand content of 300, 39 and 800 g, respectively, is beneficial for the overall rheological performance of 3D-printed geopolymer. With this mix ratio, the stacking, fluidity and viscosity recovery performance of the fresh 3D-printed geopolymer can be significantly improved.

- **3.3 Performance of PE fiber reinforced 3D-printed geopolymer**
- **3.3.1 Mix proportion**

The mix proportions of PE fiber reinforced 3D-printed geopolymer with PE fiber volume varying from 0 to 0.6% are listed in Table 10. The content of GGBS, NaOH and sand was fixed at the suggested value from the above analysis, i.e., 300, 39 and 800 g, respectively. In addition,

 incorporating fibers can deteriorate the fluidity of fresh geopolymer and thus, affect the 3D
printing performance. Therefore, extra water was added to Group 3 and Group 4 with a higher
fiber dosage of 0.4% and 0.6%, which also affected the water-to-binder ratio.

10010-10	Tuble 10 Min proportions of 12 moet remoteed 2D printed geoporymen.						
Experimental group	CCBS (a)	Fly	Sodium silicate	Water		Sand (a)	Fiber
Experimental group	00D3 (g)	ash (g)	solution (g)	(g)	NaOII (g)	Salid (g)	(%)
1	300	700	176.9	207.9	39	800	0
2	300	700	176.9	207.9	39	800	0.2
3	300	700	176.9	215.9	39	800	0.4
4	300	700	176.9	215.9	39	800	0.6

Table 10 Mix proportions of PE fiber reinforced 3D-printed geopolymer.

3.3.2 Mechanical properties

The impact of PE fiber on the mechanical performance of 3D-printed geopolymer is presented in Fig. 14. As shown in Fig. 14 (a), the compressive strength of 3D-printed geopolymer at 7 d and 28 d decreases with the incorporation of PE fibers. The more the PE fibers, the lower the compressive strength. Fortunately, the adverse effect of PE fiber on compressive strength is limited given a maximum decrease of 4.8% and 4.9% for 7-d and 28-d strength, respectively. On the one hand, the increase in PE fiber dosage leads to increased interfaces between fibers and paste [57], resulting in more weak areas in 3D-printed geopolymer. On the other hand, the ball effect of PE fibers negatively affects their restraining effect on geopolymer's lateral expansion deformation, responsible for a lessened strengthening effect on compressive strength. Therefore, the compressive strength is reduced with the increase of PE fibers.



463 Fig. 14 (a) Compressive and (b) flexural strength of PE fiber reinforced 3D-printed geopolymer.

When it comes to flexural strength, the reinforcing effect of PE fibers is significantly enhanced. It can be illustrated from Fig. 14 (b) that the incorporation of PE fiber at a dosage of 0.2% increases the 7-d and 28-d flexural strength by 19.4% and 17.7%, respectively, in comparison to the control mix (i.e., Group 1). The reason for a prominent increase in flexural strength can be traced to the crack-bridging effect of PE fiber, which helps to hinder the propagation of cracks through printing interfaces of 3D-printed geopolymer, as presented in Fig. 15. When the content of PE fibers increases from 0.2% to 0.4%, the enhancement in flexural strength is smaller. The additional water in Group 3 and Group 4 increases the water-to-binder ratio, which negatively affects the flexural strength. Thus, the additional positive effect of the increased PE fibers is offset

by the negative effect of the increased water, resulting in limited changes in both 7-d and 28-d flexural strength compared to Group 2 (i.e., PE dosage = 0.2%). Nevertheless, the toughening effect of PE fibers on 3D-printed geopolymer is still positive at a higher PE dosage of 0.4% and 0.6%.



Fig. 15 Crack-bridging of PE fibers inside 3D-printed geopolymer.

3.3.3 Rheological properties

The impact of PE fiber on rheological behavior of 3D-printed geopolymer is exhibited in Fig. 16, with H-B model fitting results listed in Table 11. As presented in Fig. 16 (a), a sharp increase can be identified in the yield stress as the content of PE fiber increases from 0% to 0.6%. Group 4 with a PE fiber content of 0.6% has the maximum yield stress, i.e., 16.82 Pa, which increases by 112.1% compared to the control group (i.e., Group 1 without PE fiber). Although Group 3 and Group 4 have a higher water content, the growth of yield stress has not been negatively affected. This indicates that increasing fiber content significantly enhances the stacking performance of 3D-printed geopolymer. As expected, given the same water content, increasing the dosage of PE fiber decreases the flowability of geopolymer slurry given an increased consistency coefficient, as observed in Fig. 16 (b). It indicates that the incorporation of PE fiber can diminish the fluidity of 3D-printed geopolymer. Fortunately, the adverse impact of PE fiber on geopolymer's flowability can be offset by increasing water content, as the consistency coefficient of Groups 3 and 4 is far lower than that of Groups 1 and 2.





493 Fig. 16 Rheological properties of PE fiber reinforced 3D-printed geopolymer: (a) yield stress, (b)
 494 consistency coefficient, (c) flow index and (d) viscosity recovery rate.



Fahla	11 H_R	model fitting	regulte of	PF fibor	rainforcad	goonolymer
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Group	Fiber content (%)	R2	SD
1	0	0.99998	0.24848
2	0.2	0.99998	0.1769
3	0.4	0.99988	0.41192
4	0.6	0.99986	0.46631

As shown in Fig. 16 (c), the flow index of 3D-printed geopolymer decreases with the addition of PE fibers given that incorporating 0.2% PE fibers reduces the flow index by 7.3% compared to Group 1 without PE fibers. In addition, increasing the content of PE fibers from 0.4% to 0.6% leads to a decrease in the flow index as well. It indicates that adding PE fibers enhances the shear-thinning behavior of 3D-printed geopolymer. As expected, incorporating extra water alleviates the shear-thinning behavior caused by adding fibers and makes geopolymer mortar behave similarly to a Newtonian fluid given that the flow index of Groups 3 and 4 is remarkably higher than that of Groups 1 and 2. Furthermore, adding PE fibers has a limited impact on the viscosity recovery performance of 3D-printed geopolymer, as the difference in the viscosity recovery rate between Group 1 and Group 2 is small. Similarly, increasing the content of PE fibers also has a limited effect on the viscosity recovery performance, with an increase of 1.3% in the viscosity recovery rate (Group 3 versus Group 4). However, incorporating extra water contributes to an enhanced viscosity recovery capability given an increased viscosity recovery rate identified in Group 3 and Group 4. This is because the addition of extra water increases the amount of free water inside 3D-printed geopolymer, providing an ion migration environment for the dissolution of raw materials and the reformation of flocculent gel during secondary shear damage [58]. Fig. 17 shows the effect of PE fibers on morphology configuration of 3D-printed specimen. It can be found that adding PE fibers leads to the appearance of transverse cracks in the lower two layers of 3D-printed geopolymer, which is because incorporating PE fibers reduces the fluidity of the geopolymer slurry. Fortunately, the incorporation of PE fibers decreases the deformation of the lower two layers of 3D-printed geopolymer caused by the extrusion of the upper structure. This can be linked to the raised yield stress of PE fiber reinforced 3D-printed geopolymer, which contributes to a better stacking performance, agreeing well with the results of rheological tests. From the above mechanical and rheological analysis, it can be concluded that the optimal fiber content is 0.6%, which will be used for further microstructural analysis.



Fig. 17 The morphology configuration of (a) 3D printed geopolymer without PE fiber and (b) PE fiber reinforced 3D-printed geopolymer at a fiber volume of 0.6%.

3.3.4 Microstructure investigation

The SEM images of PE fiber reinforced 3D-printed geopolymer after 28 days of curing are presented in Fig. 18. As observed in Fig. 18 (a), a tight bond can be identified between the unreacted fly ash particle and 3D-printed geopolymer paste with a significant amount of silica-alumina gel surrounding the fly ash particle. It indicates that the 3D-printed geopolymer prepared herein has an appropriate Si/Al ratio, which allows the silica-alumina component to dissolve, promoting the formation of silica-alumina gel. In addition, flocculation precipitates can also be characterized on the surface of the fly ash particle, which is owing to the combination of sodium silicate and water. Interestingly, a large number of micropores are observed in geopolymer mortar in addition to the inherent pores of silica-alumina gel, as presented in Fig. 18 (b). This can be linked to the incorporation of PE fibers, as adding fibers has an air-entraining effect due to fiber filling. Fig. 18 (c) shows the microstructure of the geopolymer specimen after flexural testing. Apparently, an increased flexural strength can be expected considering the effectively interlocked PE fibers, which suggests that PE fibers can serve as bridges that connect microcracks to resist the bending failure of geopolymer mortar. Fig. 18 (d) amplifies the microcracks surrounding PE fibers. These cracks may be attributed to stress concentration caused by the formation of mesopores after adding PE fibers, possibly responsible for the decreased compressive strength of PE fiber reinforced 3D-printed geopolymer.



Fig. 18 SEM images of PE fiber reinforced 3D-printed geopolymer: (a) general-state geopolymer
 mortar, (b) micropores, (c) PE fibers and (d) microcracks near PE fibers.

3.3.5 Elemental composition

Fig. 19 presents SEM-EDS results of the 28-days 3D-printed geopolymer without adding PE fibers. As shown in Fig. 19 (b) and Fig. 19 (c), the fly ash adopted in this study has a higher Al and Si content, thereby contributing to sufficient geopolymerization under alkaline conditions. The elemental composition of the gel product of 3D-printed geopolymer is presented in Fig. 19 (d). Obviously, in addition to Si and Al elements, a higher Ca content can also be characterized in the gel product, indicating that geopolymerization and hydration reaction occur simultaneously inside 3D-printed geopolymer to generate both N-A-S-H gel and C-(A)-S-H gel. The incorporation of GGBS is responsible for the hydration reaction, since it has a higher CaO content (see Table 1). The formation of hydration product, i.e., C-(A)-S-H gel, is conducive to the development of mechanical properties of geopolymer mortar [59].



Fig. 19 SEM-EDS analysis of 3D-printed geopolymer without PE fiber: (a) selected points, (b)-(d) energy spectrum of each point.

The SEM-EDS result of the 28-days 3D-printed geopolymer with a fiber content of 0.6% is demonstrated in Fig. 20. As expected, it can be found that adding PE fibers leads to a slight increase in the Si/Al ratio (from 1.57 to 2.12) but a significant increase in the Si/Ca ratio (from 0.62 to 2.49) in the gel product when comparing Fig. 19 and Fig. 20. It signifies that adding PE fibers may have a negative effect on geopolymerization but a positive effect on hydration processes. This may be because the 0.6%-volume PE fibers entangle with the reactants, i.e., fly ash and GGBS, reducing their specific surface area and thus negatively affecting the geopolymerization process. Although water serves as the medium for ion migration during geopolymerization [60], it participates in the hydration reaction. Thereupon, the additional water in Group 4 with a 0.6% PE fiber benefits the hydration reaction compared to Group 1 without PE fiber, responsible for the significant increase in the Si/Ca ratio.



Fig. 20 SEM-EDS analysis of 3D-printed geopolymer with PE fiber: (a) selected points, (b)-(d) energy spectrum of each point.

573 4. Conclusions

This study developed a novel 3D-printed geopolymer. The optimum mix proportion for 3Dprinted geopolymer was obtained by evaluating the impact of GGBS, NaOH and sand content on mechanical properties and 3D printing performance. The rheological behavior of 3D-printed geopolymer was then assessed. Moreover, PE fibers were incorporated to enhance the mechanical and rheological performance of 3D-printed geopolymer. Following conclusions can be obtained:

(1) GGBS and NaOH contents are dominant factors for compressive and flexural strength, respectively, with the optimum dosage of 300 and 39 g (or 58 g). Considering the decreased shape retention performance caused by a NaOH content of 58 g, the NaOH content of 39 g is more appropriate for 3D-printed geopolymer. For sand content, the dosage of 800 g benefits both mechanical properties and 3D printing performance. Therefore, the GGBS, NaOH and sand content of 300, 39 and 800 g, respectively, is suggested for 3D-printed geopolymer.

(2) As GGBS content increases from 100 to 300 g, the stacking performance, flowability, thixotropic behavior and viscosity recovery performance of fresh geopolymer initially increases and then decreases with the optimum dosage being 200 g. With the increase of sand and NaOH content, improved stackability, thixotropic and viscosity recovery performance can be identified. In addition, increasing sand content benefits the flowability of 3D-printed geopolymer, while an increase in NaOH content has an adverse effect on the flowability.

(3) Adding PE fibers results in a significant rise in the flexural strength of 3D-printed
geopolymer but has a minor negative influence on compressive strength. Increasing PE fiber
volume significantly improves the stacking performance and enhances the shear-thinning behavior
of 3D-printed geopolymer. From the SEM-EDS analysis, it can be found that incorporating PE
fibers is not conducive to the geopolymerization but benefits the hydration process given an
increase of Si/Al ratio and Si/Ca ratio identified in PE fiber reinforced 3D-printed geopolymer.

CRediT authorship contribution statement

Xingyi Zhu: Conceptualization, Supervision, Writing - review & editing. Jiakang Wang:
Investigation, Formal analysis, Data curation, Writing - original draft. Ming Yang: Investigation,
Formal analysis. Jianzhuang Xiao: Writing - review & editing. Yating Zhang: Formal analysis,
Writing - review & editing. Francisco A. Gilabert: Writing - review & editing.

Declaration of competing interest

603 The authors declare that they have no known competing financial interests or personal 604 relationships that could have appeared to influence the work reported in this paper.

605 Acknowledgement

The work described in this paper is supported by the National Natural Science Foundation of China (Nos. 52278455, 52311530685 and 52308452), the Shuguang Program of Shanghai Education Development Foundation and Shanghai Municipal Education Commission (21SG24), the International Cooperation Project of Science and Technology Commission of Shanghai Municipality (No. 22210710700) and the Fundamental Research Funds for the Central Universities.

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